INFLUENCE OF BEDROCK GEOLOGY AND TREE SPECIES COMPOSITION ON STREAM NITRATE CONCENTRATIONS IN MID-APPALACHIAN FORESTED WATERSHEDS

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Abstract. Although the large variations in nitrate export from forested watersheds have been attributed to a variety of natural and disturbance-related factors, baseflow nitrate concentrations in 49 mid-Appalachian forested watersheds were most strongly related to differences in bedrock geology. Within the mid-Appalachian region of Pennsylvania, Maryland and West Virginia, watersheds dominated by Pottsville and Allegheny sandstone (PVA), Catskill, Chemung, and Pocono shale and sandstone (CCP), and Mauch Chunk shale and Greenbrier limestone (MCG), respectively, exhibited significantly different low, intermediate, and high mean stream nitrate concentrations. Soil pH, soil percent N concentration (%N), soil C:N mass ratio, soil exchangeable Ca, watershed slope, and the occurrence of white ash (*Fraxinus americana* L.), sugar maple (*Acer saccharum* Marsh.), and eastern hemlock (*Tsuga canadensis* L.) were related significantly to bedrock geology type as well as stream nitrate levels. Other factors such as past land disturbances (fire and agriculture) and stand age (old-growth) typically were associated with only one bedrock geology type. However, within a bedrock geology type, past agriculture and the presence of old-growth forest may be important in explaining stream nitrate concentrations on an individual watershed basis. The basal area of black locust (*Robinia pseudoacacia* L.), a species that enhances soil nitrogen levels *via* nitrogen fixation, showed a moderate positive correlation with stream nitrate concentrations. Bedrock geology explained the most variation in winter (49%) and summer (32%) stream nitrate concentrations. Bedrock geology may have been a better predictor of stream nitrate concentrations than soil chemistry, because the geologic variation was better assessed at the regional scale of this study compared to soil chemistry, which varies at the micro-scale due to topographic, vegetation, microbial, and climatic influences. Results of this study suggest that bedrock geology is an important factor to consider when assessing forest nitrogen dynamics at a broad landscape scale.

Keywords: agriculture, black locust (*Robinia pseudoacacia* L.), C:N ratio, fire, forest, land-use history, old-growth, nitrate leaching, nitrogen saturation, water quality

1. Introduction

Significant regional variability in stream nitrate export exists among mid-Appalachian forested watersheds. DeWalle and Pionke (1996) reported that nitrate export varied by as much as 500% among forested watersheds in the region. Many factors have been cited to explain differences in nitrate export at watershed and

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regional scales, including differences in wet and dry atmospheric nitrogen deposition (Johnson and Lindberg, 1992; Dise and Wright, 1995; Aber *et al.*, 2003), soil nitrogen cycling processes and soil chemistry (Goodale and Aber, 2001; Lovett *et al.*, 2002; Ollinger *et al.*, 2002), forest species composition (Van Miegroet and Cole, 1984; Binkley and Valentine, 1991; Lewis and Likens, 2000; Lovett *et al.*, 2000), stand age (Vitousek and Reiners, 1975; Goodale and Aber, 2001), past land disturbance history (Raison, 1979; Alriksson and Olsson, 1995; Compton and Boone, 2000; Goodale *et al.*, 2000), and insect defoliation (Swank *et al.*, 1981; Webb *et al.*, 1995; Eshleman *et al.*, 1998; Drohan and DeWalle, 2002).

In the most comprehensive assessment of nitrogen cycling in North America, the Integrated Forest Study (IFS), Johnson and Lindberg (1992) reported that atmospheric nitrogen deposition rates explained only 11% of the variation in nitrate leaching from 16 watersheds. Williard *et al.* (1997) found that atmospheric deposition rates were not important in explaining differences in nitrate export from mid-Appalachian forested watersheds. Even though atmospheric wet and dry nitrogen deposition rates are relatively high in the mid-Appalachian region (9.2–11.1 kg N ha^{-1} per year), they do not differ greatly from West Virginia to northwestern Pennsylvania where regional differences in nitrate export were observed (Williard *et al.*, 1997). Lovett *et al.* (2000) also found that variations in stream nitrate concentrations were not attributable to differences in atmospheric deposition in the Catskill Mountains of southeastern New York. However, atmospheric nitrogen deposition still plays an important role in the nitrogen cycling of these forested watersheds, since chronic nitrogen deposition is the dominant external input of nitrogen into these ecosystems, especially in the northeastern United States.

Johnson and Lindberg (1992) found that soil nitrogen mineralization rates explained the most variation (44%) in nitrate export from forested IFS watersheds. Controls of soil mineralization rates include soil moisture content, temperature, C:N ratios, and pH (Alexander, 1977; Paul and Clark, 1996). These factors, in turn, are controlled by other ecosystem conditions. Soil moisture and temperature are controlled by climatic and topographic conditions. Soil C:N ratios are affected by overstory vegetation type and stand age, amount of N-fixation, and past land disturbances. Soil pH is controlled by the buffering capacity of the soil, which is influenced by bedrock geology and biogeochemical processes.

Of these underlying potential causes of stream nitrate variation, bedrock geology, past land disturbance (fire, agriculture, and logging), forest species composition, and stand age were included in the experimental design of this study. Variability in stream pH, specific electrical conductance (SEC), base cation concentrations, and alkalinity have been attributed to differences in bedrock geology (Johnson and Reynolds, 1977; Ponce *et al.*, 1979; Silsbee and Larson, 1982), though little research has examined stream nitrate and bedrock geology relationships (Dahlgren, 1994; Holloway *et al.*, 1998). In some areas of the western United States, bedrock has been shown to be a source of nitrogen, in the form of ammonium incorporated into the interlayer of minerals (muscovite and sericite) (Dahlgren, 1994;

Holloway *et al.*, 1998). We hypothesize that bedrock geology may be related to stream nitrate through its control on soil fertility, and thus soil nitrogen cycling, not direct inputs of nitrogen from bedrock as in the western United States.

Severe fires can affect long-term forest nitrogen cycling by volatilizing significant amounts of soil nitrogen (Gagnon, 1965; Grier, 1975; Raison, 1979; Hornbeck and Lawrence, 1996). Past agriculture can result in depleted or enriched long-term soil nitrogen pools depending on the degree and types of fertilization and tillage practices (Alriksson and Olsson, 1995; Compton and Boone, 2000). Logging can increase nitrate leaching to streams by reducing stand uptake rates of nitrogen and by disturbing upper soil horizons, thereby stimulating nitrogen mineralization and nitrification rates (Huttl and Schaaf, 1995). However, logging effects on stream nitrate levels are generally short term, 1–4 years, in the Appalachians (Hornbeck *et al.*, 1987; Lynch and Corbett, 1991; Dahlgren and Driscoll, 1994; Pardo *et al.*, 1995). Stand age can affect nitrate leaching because young aggrading forests generally have greater nutrient demands and nitrogen uptake rates than mature stands (Vitousek and Reiners, 1975).

Identifying ecosystem variables controlling stream nitrate variation could facilitate the regional estimation of stream nitrate export from forest land. In this study, we examined the contributions of (1) bedrock geology, (2) soil chemistry [e.g. pH, percent N concentration (%N), percent C concentration (%C), C:N mass ratio, P, and base cations], (3) past land disturbance (e.g., fire, agriculture, and logging), (4) stand age (5) overstory vegetation type, and (6) physiographic parameters (e.g., average basin slope and watershed aspect) toward explaining stream nitrate concentrations in 49 mid-Appalachian forested watersheds.

2. Methods

2.1. Study sites

The 49 watersheds were located in three regions of the mid-Appalachians: northwestern Pennsylvania (NW PA), southwestern Pennsylvania (SW PA), and northern West Virginia and western Maryland (WV MD) (Figure 1, Table I). The watersheds are 100% forested with no major disturbances during the past 60 years. Most of the watersheds are relatively small (<6 km^2) and contain first or second-order streams (Table I). Predominant overstory species across the three regions were sugar maple (*Acer saccharum* Marsh.), black cherry (*Prunus serotina* L.), and eastern hemlock (*Tsuga canadensis* L.).

Watersheds were grouped into three geologic categories: Pottsville and Allegheny sandstone (PVA), Catskill, Chemung, and Pocono shale and sandstone (CCP), and Mauch Chunk shale and Greenbrier limestone (MCG) (Figure 1, Table I), based on relative differences in published bedrock fertility and groundwater pH values. PVA, CCP, and MCP bedrock types, respectively, exhibit low,

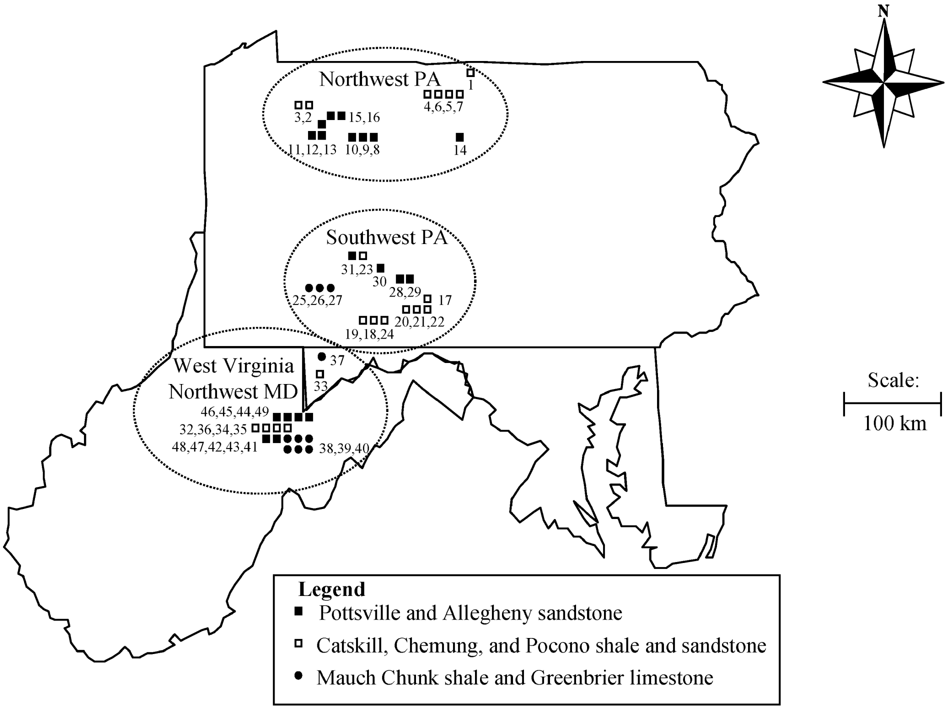


Figure 1. Locations and geology classification of the 49 study watersheds in the mid-Appalachian region of the United States. See Table I for watershed numbers and names.

intermediate, and high bedrock fertility and groundwater pH values (Ponce *et al.*, 1979; Taylor *et al.*, 1982, 1983; DeWalle *et al.*, 1987). All of the study watersheds, except for East Branch Pine Creek, were located on unglaciated terrain.

The watersheds were classified further according to past land use or disturbance history (agriculture, burned, logged, and old-growth) (Table I). Agricultural watersheds were cultivated 60–90 years ago and were then left to regenerate to forestland. Past agriculture was documented using historical aerial photographs and present day clues (old fence posts, rock piles, foundations). Burned watersheds experienced severe fires 60–90 years ago caused by the abundant slash after the clearcutting of mid-Appalachian forests in the early 1900s. Current vegetation resulted from natural regeneration. Historical fire records and maps from the Allegheny National Forest, PA, Monongahela National Forest, WV, and Buchanan State Forest, PA were examined to locate severely burned areas. The logged watersheds were cut between 60 and 90 years ago, and did not experience any subsequent severe fires, based on fire records. Stand age inventories for the Monongahela National Forest, WV, Allegheny National Forest, PA, and Buchanan State Forest, PA were used to identify old-growth watersheds. Old-growth stands were defined as any stand not harvested within the past 150 years. Old-growth watersheds were located in

TABLE I
Physical characteristics of the study watersheds

Watershed	Region[a]	Area (km^2)	Aspect	Dominant bedrock (geology category)[b]	Disturbance history
E. Branch Pine Creek	NW PA	0.860	S	Huntley Mt. (CCP)	Agriculture
Bimber Run	NW PA	0.566	SE	Shenango/Cuyahoga (CCP)	Agriculture
Rt. Branch Camp Run	NW PA	0.324	S	Shenango/Cuyahoga (CCP)	Agriculture
Jones Run	NW PA	0.702	SSE	Catskill (CCP)	Agriculture
Baker Hollow	NW PA	3.124	SSE	Catskill (CCP)	Logged
Jacob Run	NW PA	1.656	ESE	Catskill (CCP)	Logged
Sharpes Hollow	NW PA	0.757	SW	Huntley Mt. (CCP)	Logged
Red Mill Run	NW PA	3.370	SE	Pottsville (PVA)	Burned
Italian Shanty Run	NW PA	2.673	ENE	Pottsville (PVA)	Burned
Crow Run	NW PA	4.975	SW	Pottsville (PVA)	Burned
Little Salmon Creek	NW PA	0.642	S	Pottsville (PVA)	Logged
West Branch	NW PA	1.474	SE	Pottsville (PVA)	Logged
The Branch	NW PA	1.944	SW	Pottsville (PVA)	Logged
Beech Bottom Run	NW PA	0.650	NE	Pottsville (PVA)	Old-growth
West Fork Run	NW PA	3.699	SW	Pottsville (PVA)	Old-growth
East Fork Run	NW PA	6.348	SW	Pottsville (PVA)	Old-growth
Sindeldecker Branch	SW PA	2.976	E	Catskill (CCP)	Burned
Bear Gap Run	SW PA	5.629	SW	Tuscarora (CCP)	Burned
Pigeon Roost Run	SW PA	4.441	S	Tuscarora (CCP)	Burned
Bowl Run	SW PA	0.808	SSE	Catskill (CCP)	Logged
Betsey Gap Run	SW PA	2.370	ESE	Catskill (CCP)	Logged
Little Point Run	SW PA	1.662	ESE	Catskill (CCP)	Logged
Lick Run	SW PA	7.708	NE	Shenango/Oswayo (CCP)	Old-growth
Sweet Root Gap	SW PA	5.598	ESE	Juniata (CCP)	Old-growth
Little Run	SW PA	0.639	NNE	Mauch Chunk (MCG)	Agriculture
Nedrow Run	SW PA	0.990	SE	Mauch Chunk (MCG)	Agriculture
Roaring Run	SW PA	0.542	N	Mauch Chunk (MCG)	Agriculture
Gallitzen Run	SW PA	0.639	NE	Pottsville (PVA)	Logged
Ashtola Run	SW PA	1.371	W	Pottsville (PVA)	Logged
Deadlift Run	SW PA	0.960	SE	Allegheny (PVA)	Logged
Tubmill Creek	SW PA	14.005	NNE	Allegheny (PVA)	Old-growth
Clover Run	WV MD	0.188	SE	Chemung (CCP)	Agriculture
Accident Run	WV MD	0.639	SE	Pocono (CCP)	Agriculture
Fernow 4	WV MD	0.390	NNW	Catskill (CCP)	Logged
Fernow 10	WV MD	0.150	N	Catskill (CCP)	Logged
Bear Run	WV MD	1.753	SE	Chemung (CCP)	Old-growth
Little Bear Run	WV MD	0.999	NNE	Greenbrier (MCG)	Agriculture
Freeland Run	WV MD	1.284	NNW	Mauch Chunk (MCG)	Logged
East Freeland Run	WV MD	0.402	W	Mauch Chunk (MCG)	Logged
Salamander Run	WV MD	1.063	NW	Mauch Chunk (MCG)	Logged
Karly Run	WV MD	0.279	SE	Mauch Chunk (MCG)	Logged
West Three Spring	WV MD	0.117	E	Mauch Chunk (MCG)	Old-growth
East Three Spring	WV MD	0.115	SE	Mauch Chunk (MCG)	Old-growth
Engine Run	WV MD	5.243	SSE	Pottsville (PVA)	Burned
Shays Run	WV MD	6.030	S	Pottsville (PVA)	Burned
Lindy Run	WV MD	5.710	SE	Pottsville (PVA)	Burned
Otter Run	WV MD	0.481	E	Pottsville (PVA)	Logged
Condon Run	WV MD	3.472	E	Pottsville (PVA)	Logged
Red Brush Run	WV MD	5.507	NNW	Pottsville (PVA)	Logged

[a]Region. NW PA: northwestern Pennsylvania; SW PA: southwestern Pennsylvania; WV MD: northern West Virginia and western Maryland.

[b]Geology Category. CCP: Catskill, Chemung, and Pocono shale and sandstone; PVA: Pottsville and Allegheny sandstone; MCG: Mauch Chunk shale and Greenbrier limestone.

the Tionesta Scenic and Natural Area, PA, the Sweet Root Natural Area, PA, the Rachelwood Preserve, PA, and adjacent to Otter Creek Wilderness, WV.

It was not possible to find each of the watershed types in each geology category. Therefore, an unbalanced experimental design resulted.

2.2. Field measurements

Stream water was grab sampled from all 49 watersheds at baseflow conditions from August 18 to 22, 1997 (summer) and March 11 to 14, 1998 (winter). Grab samples were analyzed for dissolved nitrate and ammonium at the Water Analysis Laboratory at The Pennsylvania State University using cadmium reduction and automated phenate methods, respectively (American Public Health Association, 1995). Stream pH and SEC were measured in the field using calibrated, portable meters (pHTestr 3 and TDSTestrby Oakton Inc., Singapore). Stream temperature was measured using a calibrated mercury thermometer.

Study watersheds were delineated on USGS 7.5-min quadrangle topographic maps. Catchment area and average basin slope were calculated using the delineated watershed boundaries. Watershed area was determined using a digital planimeter (Sokkia Corp., Overland Park, KS). Average basin slope was calculated using the Wentworth (1930) line-intersection method. Bedrock geology was determined with quadrangle geology maps (Reger, 1923, 1931; Maryland Geological Survey, 1953; Berg and Dodge, 1981). Basal area estimates of tree species were determined by point sampling with a 10-factor wedge prism on 48 of 49 the study watersheds (Wenger, 1984). Red Brush Run in West Virginia was not sampled for tree basal area because the landowners did not grant access. Eight points were sampled on each watershed with 4 in the riparian zone and 4 on the mid-slope. Riparian zone points were spaced evenly along the length of the stream channel. Two mid-slope points were sampled on each of the two side slopes along the main channel.

Soil chemistry parameters were measured in August 1998 on a subset of 33 of the 49 watersheds. The 33 watersheds were chosen to obtain at least two experimental units (catchments) within each land use type (burned, agriculture, logged, old-growth) in each of the three regions. On each watershed, three 16-m sampling transects were located by watershed position and elevation. Transect 1 was located near the watershed mouth (stream water sampling point) at a low elevation. Transect 2 was located near the middle of the watershed at a mid-slope elevation. Transect 3 was located in the headwaters of the watershed at a ridge top elevation. Nine soil sampling points were spaced at 2 m intervals along each sampling transect for a total of 27 soil sampling points per watershed. At each soil sampling point, the entire organic horizon was sampled with a sharpshooter shovel and the top 10 cm of mineral soil was sampled with a 10 cm diameter soil corer. Organic and mineral soil samples were transported to The Pennsylvania State University, Agricultural Analytical Laboratory for analyses. Exchangeable Ca, Mg, and K and labile, mineralized P were determined with the Mehlich 3 method (Wolfe and Beegle, 1995). Exchangeable acidity was extracted and measured with the Shoemaker, McLean, and Pratt (SMP) buffer method (Sims and Eckert, 1995). Soil pH was measured in a slurry (5 g soil:5 ml distilled water) using an electronic pH meter (Sims and Eckert, 1995). Effective cation exchange capacity (CEC) was calculated by summing the exchangeable Ca, Mg, K, and acidity (Ross, 1995). Organic and mineral soil were analyzed for total C and N at the USDA Forest Service's Timber and Watershed Laboratory in Parsons, WV using an organic elemental analyzer (Carlo Erba NA 1500 CNS Analyzer, Valencia, CA) (Baccanti *et al.*, 1993).

2.3. Statistical methods

Four data sets were analyzed statistically: stream chemistry of 49 watersheds, soil chemistry of 33 watersheds, physiographic parameters of 49 watersheds, and vegetation inventory of 48 watersheds. The SAS Institute Inc. statistical package, Version 7 for Windows (1998), was used to analyze the data sets. Each data set was analyzed to determine if the error terms were normally distributed and homogeneous (assumptions underlying ANOVA). Normal probability plots and Shapiro–Wilk test statistics (SAS Institute Inc., 1985) confirmed that all the data sets were normally distributed. Bartlett's tests (SAS Institute Inc., 1985) showed error variances for the ANOVA models to be relatively homogeneous. Given the normal distribution of data and the homogeneity of error variance, no data transformations were required for subsequent analysis of variance tests (ANOVA).

ANOVA models for stream chemistry, soil chemistry, physiographic, and vegetation inventory data sets included the following terms: (1) geographic region (NW PA, SW PA, and MD WV), (2) geology category (PVA, CCP, and MCG), and (3) land use (burned, agriculture, logged, and old-growth). Tukey's studentized range test (HSD) was added to each model to test for significant differences among the single factors: region, geology category, and land use for each dependent variable. The stream chemistry ANOVA model was run for summer and winter separately. Pearson correlation tests were run among the stream chemistry, soil chemistry, physiographic, and vegetation inventory data sets. A maximum R^2 improvement stepwise regression model (SAS Institute Inc., 1985) also was constructed to determine the factors that best predicted stream nitrate concentrations. The three geology and four land use categories were included in the stepwise regression model as dummy variables. All tests of significance were made at the $\alpha = 0.05$ confidence level.

3. Results and Discussion

Stream ammonium-N concentrations were at or near the detection limit (0.005 mg L^{-1} NH_4^+-N) in most of the 49 study watersheds, but as expected, nitrate concentrations varied widely (<0.005–1.702 mg L^{-1} nitrate-N). However, stream nitrate concentrations did not vary significantly among geographic regions (NW PA, SW PA, and WV MD) (Figure 1).

An examination of stream nitrate change in rank order over time can help assess whether a two-time baseflow survey serves as an adequate representation of stream nitrate concentrations. The median change in rank order for the 47 sampled watersheds between August 1997 and March 1998 was 6 with a 95% confidence interval of ± 2, using a non-parametric sign test with an S table (Noether, 1991). Thus, the 47 watersheds exhibited little change in rank, which indicates that a two-time survey can serve as an adequate index to stream nitrate concentrations. Also, Edwards *et al.* (2004) showed that relatively low intensity stream sampling (quarterly) in WV could be used to predict actual stream nitrate loads from forested watersheds as accurately as more intensive sampling (weekly) because of the small fluctuation in nitrate concentrations over flow and time.

Two of the 49 watersheds included in the baseflow surveys were intensively monitored experimental watersheds in the Fernow Experimental Forest, Fernow 4 and Fernow 10. Our summer nitrate-N concentrations from Fernow 4 and Fernow 10 (0.770 and 0.394 mg L^{-1}, respectively) and winter concentrations (0.731 and 0.038 mg L^{-1}, respectively) fell well within the range of weekly nitrate-N concentrations from water years 1996 to 1999 and closely approximated the mean nitrate-N concentration from these water years (Table II). These results provide additional

TABLE II

Stream nitrate-N concentrations (mg L^{-1}) for watersheds 4 and 10 on the Fernow Experimental Forest

Water year	Mean	S.D.	Minimum	Maximum
WS4 growing season NO_3-N				
1997	0.653	0.016	0.51	0.86
1998	0.713	0.026	0.50	1.00
1996–1999	0.685	0.015	0.50	1.48
WS4 dormant season NO_3-N				
1997	0.765	0.009	0.69	0.87
1998	0.904	0.023	0.67	1.09
1996–1999	0.787	0.012	0.60	1.09
WS10 growing season NO_3-N				
1997	0.195	0.017	0.11	0.29
1998	0.311	0.052	0.15	0.62
1996–1999	0.224	0.021	0	0.68
WS10 dormant season NO_3-N				
1997	0.121	0.016	0	0.19
1998	0.273	0.073	0.11	1.07
1996–1999	0.188	0.028	0	1.07

support for the adequacy of two-time baseflow surveys to characterize the stream nitrate concentrations.

3.1. Explaining stream nitrate variation

3.1.1. *Geology*

The significant variability in stream nitrate concentrations among the study watersheds was related to differences in bedrock geology (Table III). The MCG, CCP, and PVA bedrock watersheds had the highest, intermediate, and lowest mean summer and winter stream nitrate-N concentrations, respectively (Figure 2). Ponce *et al.* (1979) found that stream nitrate varied by bedrock type in the Little Black Fork watershed in West Virginia. Stream water associated with Greenbrier limestone had the highest mean nitrate-N concentration (1.31 mg L^{-1}), and those

TABLE III

Mean stream chemistry, soil chemistry, and physiographic parameter values for the three geology categories

Parameter	PVA	CCP	MCG
Summer stream NO_3-N (mg L^{-1})	0.162 a*	0.424 b	0.750 c
Winter stream NO_3-N (mg L^{-1})	0.174 a	0.398 b	0.940 c
Summer stream pH	5.10 a	6.59 b	6.96 b
Winter stream pH	5.03 a	6.23 b	6.56 b
Summer stream SEC (μS cm^{-1})	36.1 a	36.0 a	46.5 a
Winter stream SEC (μS cm^{-1})	26.8 a	28.5 a	32.0 a
C in organic soil (%)	18.980 a	14.055 b	16.185 ab
C in mineral soil (%)	4.067 a	3.979 a	5.042 b
N in organic soil (%)	0.895 a	0.733 b	0.917 a
N in mineral soil (%)	0.262 a	0.265 a	0.382 b
C:N ratio of organic soil	20.720 a	19.013 b	16.918 c
C:N ratio of mineral soil	15.603 a	15.062 a	13.394 b
Organic soil P (meq. kg^{-1})	0.0036 a	0.0062 b	0.0046 ab
Mineral soil P (meq. kg^{-1})	0.0026 a	0.0041 a	0.0029 a
Organic soil Ca (meq. kg^{-1})	0.124 a	0.168 b	0.226 c
Mineral soil Ca (meq. kg^{-1})	0.072 a	0.080 ab	0.105 b
Organic soil pH	3.59 a	3.97 b	4.06 b
Mineral soil pH	3.73 a	4.01 b	4.01 b
Average basin slope (°)	5.955 a	12.998 b	17.209 b
Area (km^2)	3.642 a	2.115 ab	0.643 b

*Parameter means with different letters across the three geology categories are significantly different at $\alpha = 0.05$ using Tukey's HSD mean separation procedure.

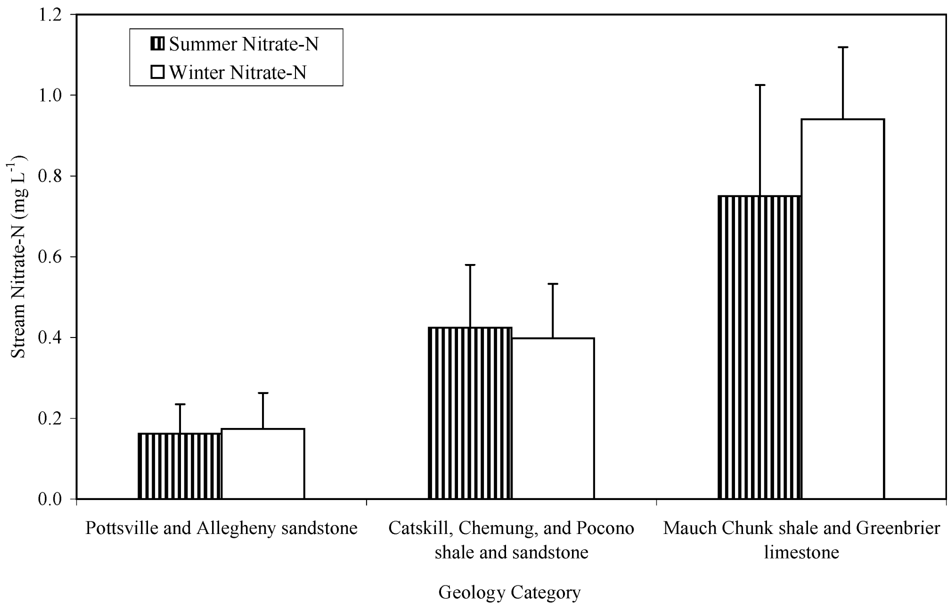


Figure 2. Mean summer and winter stream nitrate-N concentrations for the three geology categories.

associated with Mauch Chunk shale also yielded water relatively enriched in nitrate-N (1.02 mg L^{-1}). The Catskill shale and sandstone in Little Black Fork watershed yielded water with a lower mean nitrate-N concentration (0.69 mg L^{-1}). These findings and concentrations are consistent with our data for MCG and CCP geologies. By contrast, Ponce *et al.* (1979) found that stream water from Pottsville sandstone yielded stream water with a mean nitrate-N concentration of 1.04 mg L^{-1}, which was significantly higher than the mean nitrate-N concentrations we found (0.162 and 0.174 mg L^{-1}). The mean nitrate-N concentration from Pottsville sandstone reported by Ponce *et al.* (1979) (1.04 mg L^{-1}) was similar to the nitrate-N concentration from Mauch Chunk shale (1.02 mg L^{-1}) in our study. Mauch Chunk shale may influence water thought to originate from Pottsville sandstone because it is found beneath the Pottsville layer. At Laurel Hill, PA, Goyne (1998) showed that the mean soil solution nitrate-N concentration in A-horizons derived from Mauch Chunk shale (0.511 mg L^{-1}) was significantly greater than in A-horizons derived from Pottsville sandstone (0.167 mg L^{-1}). This relationship follows the stream nitrate differences we observed between MCG and PVA watersheds.

Other studies did not show a relationship between stream nitrate and bedrock type (Silsbee and Larson, 1982; Johnson and Reynolds, 1977); however, neither of these two surveys included a geologic strata that produced relatively high pH waters like MCG. Silsbee and Larson (1982) analyzed stream water quality in two dominant geology types in the Great Smokey Mountains National Park. Nitrate-N was only slightly higher in waters from the Anakeesta formation (0.856 mg L^{-1}), which is composed of slate, phyllite and/or schist with significant amounts of pyrite, compared to the Great Smokey Group (0.673 mg L^{-1}), which is composed of thick-bedded sandstone containing quartz and feldspars. Johnson and Reynolds (1977) found similar stream nitrate concentrations in stream water from plutonic bedrock (quartz, granite) and from metamorphic and sedimentary bedrock (schist and slate).

In forested watersheds in the western United States, Dahlgren (1994) and Holloway *et al.* (1998) found that muscovite and sericite minerals in bedrock provided a significant source of nitrogen as interlayer ammonium. Although we did not measure the nitrogen content of bedrock in our study, geologic literature does not indicate that any of our bedrock types contain significant quantities of interlayer ammonium or other nitrogen forms. Consequently, bedrock geology must control stream water nitrate by an indirect mechanism in which bedrock determines soil fertility, which influences soil nitrogen cycling and nitrate leaching.

3.1.2. *Past Land Disturbances*

Past land disturbances did not explain a significant amount of nitrate variation during winter. During summer, watersheds with a past agricultural history yielded significantly greater mean nitrate-N concentrations (0.812 mg L^{-1}) compared to the three other land use histories (burned = 0.091 mg L^{-1}, logged = 0.308 mg L^{-1}, old-growth = 0.423 mg L^{-1}). However, agricultural watersheds occurred only within the two most fertile geology categories (CCP and MCG). Among the agricultural watersheds, the MCG geology watersheds had a significantly higher mean nitrate-N concentration (1.136 mg L^{-1}) than the CCP geology watersheds (0.596 mg L^{-1}) in a paired *t*-test. As a result, past land use differences did not appear to account for any of the stream nitrate variation beyond that which was already explained by geology.

3.1.3. *Physiographic Parameters*

Stream nitrate did not differ significantly by watershed aspect, the physiographic parameter we predicted would most likely affect stream nitrate concentrations due to its microclimatic effects on soil temperature. However, winter stream nitrate was correlated positively with average basin slope ($r = 0.417$, $p = 0.003$) and negatively with watershed area ($r = -0.310$, $p = 0.030$). Summer stream nitrate also was correlated negatively with watershed area ($r = -0.294$, $p = 0.042$). In the ANOVA model, average basin slope varied by geology category in the same manner as stream nitrate-N (Table III). The PVA geology watersheds were located primarily on the top of slopes on broad, flat plateaus, which resulted in the significantly lower average basin slope for this geology type. The significant negative correlation between watershed area and stream nitrate was also likely a function of geology. The PVA bedrock watersheds were larger in area, due to these expansive plateaus, suggesting that the correlations between average basin slope, watershed area and stream nitrate may be a function of geologic differences that affected landform, rather than direct relationships.

3.1.4. *Vegetation*

One would expect vegetation to affect nitrate leaching primarily during the growing season. Summer stream nitrate concentrations were correlated positively with the mean watershed (riparian zone and mid-slope) basal area of sugar maple (*Acer saccharum* Marsh.), white ash (*Fraxinus americana* L.), and black locust (*Robinia pseudoacacia* L.) and negatively correlated with the mean watershed basal area of eastern hemlock (*Tsuga canadensis* L.) (Table IV). Riparian zone basal areas of each of the four species were correlated better with summer stream nitrate concentrations than mid-slope basal areas. This was likely due to the deeper and more fertile riparian soils having a greater influence on nitrogen cycling and transport compared to the mid-slope soils.

This study did not yield a significant correlation between red oak (*Quercus rubra* L.) and stream nitrate concentrations (Table IV), in contrast to studies by Lovett *et al.* (2000) in the Catskill Mountains of New York and Lewis and Likens (2000) in the Allegheny National Forest in northwestern PA. Lovett *et al.* (2000) analyzed nitrate concentrations from 39 streams and found the three lowest were from watersheds dominated by red oak; the five highest were from watersheds with no oaks. Lovett *et al.*'s (2000) study area was glaciated, resulting in relatively homogeneous soil fertility characteristics among the study watersheds. Thus, tree species composition will likely have a greater influence on nitrate leaching from these watersheds compared to our unglaciated study region. Lewis and Likens (2000) finding of low stream nitrate concentrations in watersheds containing red oak may be attributed to the relative abundance of acidic bedrock (Pottsville) in those Allegheny National Forest watersheds.

TABLE IV

Pearson correlation coefficients between summer stream nitrate concentrations and mean watershed basal area of overstory species on 48 study watersheds

	Summer stream nitrate concentrations	
Overstory species (basal area)	Correlation coefficient (r)	p value
Sugar maple	0.411	0.004
Black locust	0.410	0.004
White ash	0.305	0.037
Eastern hemlock	−0.282	0.055
Red oak	0.148	0.319
Birch	−0.137	0.358
American beech	−0.104	0.486
Red maple	−0.096	0.521
Black cherry	−0.029	0.845
Yellow poplar	−0.028	0.854

Of the four species correlated with summer stream nitrate concentrations, sugar maple, white ash, and eastern hemlock each covaried with bedrock geology. The MCG, CCP, PVA geology watersheds had the highest, intermediate, and lowest mean watershed basal areas of both sugar maple and white ash, respectively. Sugar maple and white ash are usually more prevalent on relatively fertile sites (MCG) (Godman *et al.*, 1990; Schlesinger, 1990). Watersheds containing PVA geology had significantly greater mean basal area of eastern hemlock compared to watersheds with other geology types. Eastern hemlock is associated most commonly with acidic soils (Godman and Lancaster, 1990).

Of the tree species correlated with stream nitrate, only black locust occurrence was not related to bedrock geology. Black locust is one of the few eastern United States forest species that support symbiotic nitrogen fixation. Danso *et al.* (1995) estimated that field-grown black locust in Austria fixed 110 kg N ha^{-1} per year. Nitrogen fixation rates in eastern United States forests may be even greater, since the growing season in the eastern United States is approximately 1–2 months longer than in Austria. In the southern Appalachians, Montagnini *et al.* (1986) found soils beneath black locust had greater mineralization and nitrification rates than surrounding soils under different vegetative cover, because of higher soil N pools. This can lead to greater soil solution nitrate concentrations underneath black locust stands (Montagnini *et al.*, 1986, 1991), and, as a result, higher stream nitrate concentrations. Therefore, the relative abundance of black locust on the study watersheds may help explain some of the additional variation in stream nitrate concentrations beyond that attributable to geology.

Black locust was found on 10 of the 48 watersheds inventoried for vegetation, but was a relatively minor stand component (2.9% of the total mean watershed basal area) of those 10 watersheds. While we did not measure soil or solution chemistry beneath black locust stands or individual trees, the significant correlation between the mean watershed basal area of black locust and stream nitrate concentrations indicates that black locust may have a significant secondary effect on stream nitrate at the watershed scale. Relatively high N-fixation rates by black locust (Danso *et al.*, 1995) may mean that even isolated stands of black locust can significantly increase nitrate leaching to streams. Stednick and Kern (1992) found that nitrate concentrations in stream water were greatest when another nitrogen-fixer, red alder (*Alnus rubra* Bong.) was abundant in the riparian zones that contributed stream water, even if alder did not cover a substantial portion of the watershed.

3.1.5. *Soil Chemistry*

Summer stream nitrate concentrations were correlated significantly with organic and mineral soil exchangeable calcium ($r = 0.438$, $p = 0.011$), pH ($r = 0.374$, $p = 0.032$), and C:N ratios ($r = -0.401$, $p = 0.021$) on 33 watersheds. Winter stream nitrate concentrations were correlated with organic and mineral soil %N ($r = 0.397$, $p = 0.022$) and C:N ratios ($r = -0.398$, $p = 0.022$). All of these soil chemistry parameters affect N mineralization and nitrification rates, and thus, nitrate leaching to streams (Norris *et al.*, 1991; Paul and Clark, 1996; Williard *et al.*, 1997; Gundersen *et al.*, 1998). Dise *et al.* (1998) and Gundersen *et al.* (1998) found that organic soil C:N ratios were correlated negatively with stream nitrate levels across a large number (111 and 33, respectively) of European forested watersheds. Lovett *et al.* (2002) showed also that organic soil C:N ratios were a significant predictor of stream nitrate concentrations from 39 forested watersheds in the Catskill region of New York, United States. High soil C:N ratios result in strong heterotrophic soil microbe demand for N, leaving less N available for nitrifying microbes and subsequent nitrate leaching (Riha *et al.*, 1986; Schimel and Firestone, 1989). Thus, at C:N ratios >30, net immobilization of nitrogen usually occurs, while C:N ratios <20 generally result in net mineralization (Alexander, 1977). All the study watersheds had organic and mineral soil C:N ratios <30, with most <20. The positive correlation between soil pH and stream nitrate was expected, given that decreases in soil pH have been shown to depress N mineralization and nitrification rates, especially at pH levels below 5.0 (Alexander, 1977; Paul and Clark, 1996).

Exchangeable calcium levels may affect inorganic nitrogen cycling rates beyond indirectly affecting acidity. Calcium is an essential element utilized in the structure and regulatory functions of bacterial cells (Norris *et al.*, 1991; Smith, 1995). Norris *et al.* (1991) reported that low calcium levels can limit the growth rates of several types of bacteria, including species of *Azotobacter*, the primary group of N-fixing bacteria. Thus, low calcium concentrations could limit N-fixation rates, reducing available N to nitrifying microbes. Low calcium also may directly limit the growth of *Nitrosomonas* and *Nitrobacter* bacteria and/or fungi responsible for nitrification.

Organic and mineral soil exchangeable calcium, pH, %N, and C:N ratios varied by geology category, in the same manner as stream nitrate-N concentrations (Table III). The PVA, CCP, and MCG geology categories generally had the lowest, intermediate, and highest Ca, pH, and %N, respectively in both organic and mineral soil. The only exception was that PVA geology watersheds had significantly higher %N in the organic soil than CCP geology watersheds (Table III), probably due to lower mineralization rates of N in the more acidic soils derived from the PVA bedrock. PVA, CCP, and MCG watersheds had the highest, intermediate, and lowest organic and mineral soil C:N ratios, respectively. Lower C:N ratios in the least acidic geology types (MCG) likely are due to more rapid decomposition and cycling of fresh litter.

3.2. Fernow 4 watershed and nitrogen saturation

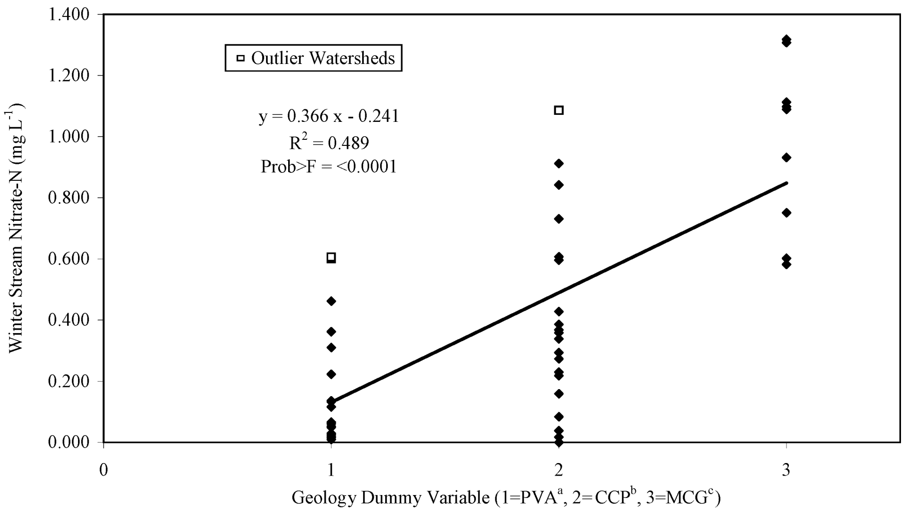
Our survey of 49 streams included Fernow 4, a watershed that has exported relatively high amounts of nitrate for the past two decades (Adams *et al.*, 1993). On Fernow 4, stream nitrate-N outputs (5.1 kg ha^{-1} per year) are nearly equal to nitrate-N bulk deposition inputs (5.0 kg ha^{-1} per year) and the stream nitrate outputs show little seasonal variation (Adams *et al.*, 1993; P. Edwards, personal communication), which are both indicators of nitrogen saturation (Peterjohn *et al.*, 1996; Gilliam *et al.*, 1996). Nitrogen saturation can be defined generally as a forest ecosystem condition where nitrogen is supplied in excess of microbial and vegetative demand (Agren and Bosatta, 1988; Aber *et al.*, 1989, 1998). In fact, Fernow 4 has been cited as the best example of a stage 2 nitrogen saturated watershed in the northeastern United States, since the watershed exhibits elevated year round nitrate concentrations (Stoddard, 1994; Peterjohn *et al.*, 1996; Fenn *et al.*, 1998).

Among CCP watersheds, Fernow 4 was at the high end of the distribution of stream nitrate concentrations. In the winter and summer baseflow surveys, Fernow 4 had the 11th and seventh highest stream nitrate-N concentration (0.731 and 0.770 mg L^{-1}, respectively) of the 49 and 48 watersheds sampled. Given the number of watersheds that had greater stream nitrate concentrations than Fernow 4, nitrogen saturation may be more prevalent in the mid-Appalachian region than previously thought. Williard *et al.* (2003) conducted more localized summer and fall stream nitrate surveys of forested watersheds within 10 km of Fernow 4 and found that nearly half of the 27 streams sampled had greater stream nitrate concentrations than Fernow 4, suggesting that nitrogen saturation is a relatively common condition within that locality.

3.3. Predicting stream nitrate concentrations

Maximum R^2 stepwise regression models containing geology dummy variables (PVA = 1, CCP = 2, MCG = 3), land use dummy variables (burned = 1, agricultural = 2, logged = 3, old-growth = 4), organic and mineral soil chemistry, vegetation, and physiographic parameters were constructed to determine which factors best predicted winter and summer stream nitrate concentrations. Geology categories were arranged from high to low acidity. Land uses were arranged from most severe to least severe historical disturbance. Geology dummy variables were the first parameters to enter the stepwise regressions of winter and summer stream nitrate. The geology dummy variables alone explained 49% of the variation in winter stream nitrate-N concentrations (Figure 3). Excluding parameters correlated with geology (soil chemistry, physiographic parameters, and some vegetation types), no other variables were significant additions to the regression model.

Three watersheds (East Fork, West Fork, and Accident Run) in Figure 3 may be termed outlier points, since their nitrate-N concentrations were greater than two standard deviations from the mean of their geology category. These watersheds were on the high end of the stream nitrate distributions within the PVA and CCP geology categories. Accident Run, in the CCP geology category, was a past agricultural watershed, indicating that past farming may affect nitrate leaching on individual watershed basis. The two outlier watersheds in the PVA geology category were both old-growth watersheds, suggesting that stand age also may be important in explaining stream nitrate concentrations from individual watersheds.



[a]PVA = Pottsville and Allegheny sandstone
[b]CCP = Catskill, Chemung, and Pocono shale and sandstone
[c]MCG = Mauch Chunk shale and Greenbrier limestone

Figure 3. Winter stream nitrate-N concentrations versus the three geology categories.

Also, the three outlier watersheds were all south-facing. South-facing watersheds receive more solar radiation, resulting in higher soil temperatures that may stimulate N-mineralization and nitrification rates, and consequently, nitrate leaching. Thus, high nitrate leaching rates on the outlier watersheds may be due partially to watershed aspect. Average basin slope and dominant overstory vegetation did not show any consistent relationships among the three outlier watersheds.

One could argue that soil chemistry differences are a more direct cause of stream nitrate variation than geology. Parameters such as C:N ratios and soil pH have been shown to directly affect the nitrate production in the soil and, thus, are more responsible for differences in nitrate leaching to streams. Soil pH was not a significant parameter in any winter regression models. When only organic and mineral soil chemistry parameters were included in a stepwise regression model for winter stream nitrate, C:N ratios explained the most variation (16%) in stream nitrate. The best two-parameter model included C:N ratios and %N, which together explained 29% of the variation in winter stream nitrate. Neither of these soil chemistry based models approached the predictive power of the geology model for winter stream nitrate (49%). This may be a function of geology being more accurately represented within the large regional scope of the study, compared to soil chemistry, which varies significantly at the micro-scale.

Summer stream nitrate predictions yielded similar results. In a stepwise regression, geology explained the most variation (32%) in stream nitrate. Basal area of black locust joined geology in a significant two-variable model, explaining 40% of the variation in summer stream nitrate (Figure 4). Black locust, a nitrogen fixing

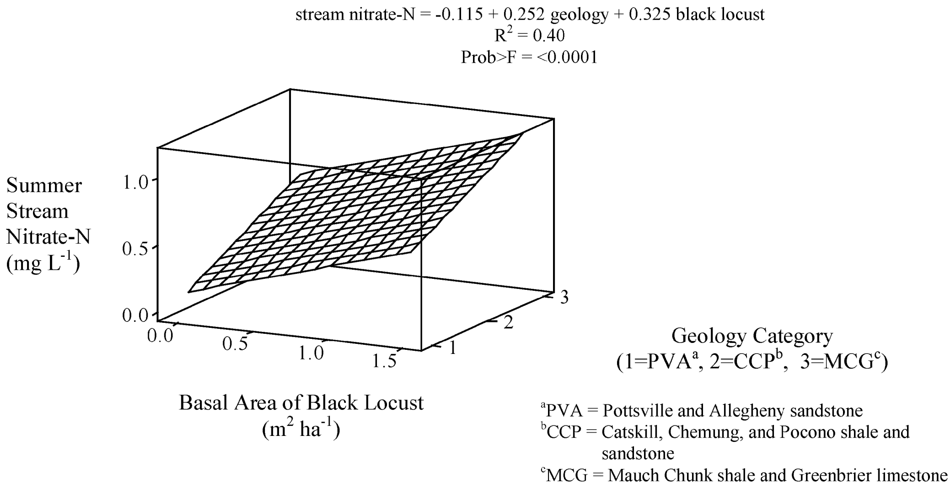


Figure 4. Summer stream nitrate-N concentrations versus the three geology categories and the basal area of black locust.

species, had an additional effect on nitrate leaching beyond the effects of geology, since it was not related to differences in geology.

Organic and mineral soil chemistry parameters did not predict summer stream nitrate concentrations as well as geology. Of the soil chemistry variables, exchangeable soil calcium was the single soil factor that explained the most variation (19%) in summer stream nitrate. The best two-parameter soil chemistry model included C:N ratios and mineralized phosphorus, which together explained 27% of the variation.

There are several factors that were not assessed in this study that could potentially account for some of the unexplained variation in stream nitrate concentrations including differences in denitrification, in-stream N processing, and insect defoliation among the study watersheds. Riparian denitrification rates can be highly variable within a watershed and among watersheds, given differences groundwater flow paths and labile carbon sources (Cooper, 1990; Hill *et al.*, 2000). Nitrogen uptake and retention in streams can be related to a variety of factors that differ among headwater streams including the amount of woody debris, leaf litter inputs, and shading (Vannote *et al.*, 1980; Mullholland *et al.*, 2000). Insect defoliations have been shown to significantly increase stream nitrate concentrations in the short-term (Swank *et al.*, 1981; Eshleman *et al.*, 1998), but may result in lower stream nitrate concentrations in the long term (Drohan and DeWalle, 2002).

4. Conclusions

We found bedrock geology to be the best predictor of summer and winter stream nitrate concentrations from 49 mid-Appalachian forested watersheds. Soil chemical parameters (pH, Ca, P, %N, and C:N) were not as important in explaining stream water nitrate. This may be because geology is more accurately mapped regionally than soils, and geologic chemistry is not as spatially variable as soil chemistry. The basal area of black locust, a nitrogen fixer, was a significant secondary predictor of summer stream nitrate. While black locust trees were not widely distributed, their presence in the riparian zone or in streamflow contributing areas appears to be sufficient to affect stream nitrate during the growing season. On an individual watershed basis, past land disturbances (agriculture) and stand age (old-growth) may be important in explaining stream nitrate concentrations. The portion of unexplained variation in stream nitrate concentrations may be attributed to differences in denitrification, hydrologic flow paths, in-stream N processing, and insect defoliation among the watersheds, which were not measured in this study and are difficult to assess at a regional scale. Our findings suggest that bedrock geology is an important factor to consider when explaining stream nitrate variation from forested watersheds, especially in unglaciated regions.

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